

Structural and magnetic behavior of the $S=2$ layered ferromagnet CsMnF_4 under hydrostatic pressure

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Pressure-induced transformations in the structural and magnetic properties of CsMnF_4 are reported. This behavior is analyzed in the framework of magnetostructural correlations within the layered perovskite AMnF_4 ($A=\text{Cs,Rb,K}$) series by using magnetic susceptibility and synchrotron x-ray powder-diffraction techniques as a function of temperature and hydrostatic pressure.

This work is part of a research program aimed at studying the magnetostructural correlations within the family of layered Mn^{3+} compounds AMnF_4 ($A=\text{Cs,Rb,K}$).^{1,2} While the Cs derivative is a model example of a layer ferromagnet that orders at $T_c=18.9$ K, the Rb and K derivatives order as antiferromagnets at, respectively, 3.7 and 5.2 K. CsMnF_4 crystallizes in the tetragonal space group $P4/n$ with $a=7.9440(6)$ Å and $c=6.3376(9)$ Å at room temperature.^{1,3} The spatial arrangement of the atoms consist of layers of $[\text{MnF}_2\text{F}_{4/2}]^-$ corner-sharing octahedra separated by Cs atoms and is related to the well-known layered-perovskite structures of TlAlF_4 type (see inset in Fig. 2). Throughout this work, we have adopted the convention of taking the c axis perpendicular to the layers.

The nuclear and magnetic structures of these compounds have been determined by neutron-powder-diffraction experiments carried out between 1.5 K and room temperature. No structural phase transitions were detected in this range. Although KMnF_4 clearly crystallizes in the monoclinic space group $P2_1/a$ with $a=7.7062(2)$ Å, $b=7.6568(2)$ Å, $c=5.7889(1)$ Å and $\beta=90.432(2)^\circ$, this is not so clear for RbMnF_4 . This pseudosymmetric compound has been refined in the orthorhombic space group $Pmab$ [$a=7.8051(8)$ Å, $b=7.7744(8)$ Å, and $c=6.0432(6)$ Å] and in the monoclinic space group $P2_1/a$ [$a=7.8119(4)$ Å, $b=7.7761(4)$ Å, $c=6.0469(3)$ Å, and $\beta=90.443(4)^\circ$]. Structural refinements using neutron diffraction data seem to indicate that the description following the monoclinic space group would be more appropriate.^{1,3}

From the magnetic point of view the decrease of α , the superexchange angle $\text{Mn}-F_{\text{eq}}-\text{Mn}$, along the members of the series from $A=\text{Cs}$ to $A=\text{K}$, goes parallel to the reduction of (i) the crystal symmetry, (ii) the volume of the unit cell, and (iii) the radius of the alkaline ion. As the size of the alkaline ion decreases, the layers get closer and electrostatic forces

tend to rotate the $[\text{MnF}_2\text{F}_{4/2}]^-$ octahedra within the layers. This results in a decrease of α , a dramatic change in the magnetic properties (e.g., from ferromagnetic to antiferromagnetic) and a reduction of the crystal symmetry of these systems.¹

An analogous, although more continuous, method of varying the interlayer spacing is to apply hydrostatic pressure to a sample of CsMnF_4 . We here report on the high pressure measurements made on this material by means of two independent techniques. The first using energy-dispersive powder diffraction (EDPD) to follow the effect of pressure on the crystal structure and the second using magnetic susceptibility to follow the effect of pressure on the magnetic properties.

Polycrystalline CsMnF_4 was prepared by controlled dehydration of $\text{CsMnF}_4 \cdot 2\text{H}_2\text{O}$ at 120 °C. The hydrated compound was synthesized following previously described methods.^{4,5} The samples were found to be free of impurities after being checked by conventional x-ray powder-diffraction methods.

Powder-diffraction spectra were collected at a series of different static pressures using the EDPD facility at the Daresbury Laboratory Synchrotron Radiation Source (SRS).^{6,7} The EDPD method uses a polychromatic beam of x-rays and a solid state detector set at a fixed scattering angle. After each set of three or four diffraction patterns, the scattering angle was calibrated by using silicon as standard. The values obtained moved from $2\theta=5.760^\circ$ to $2\theta=5.770^\circ$ between the ambient and the highest pressure patterns, respectively. The fixed geometry makes it straightforward to obtain good quality spectra, in a few minutes, from a sample contained in a high pressure cell with little or no contamination from gasketing material. In this case each pattern was collected for about 15 minutes. The EDPD method has the disadvantage that the momentum resolution

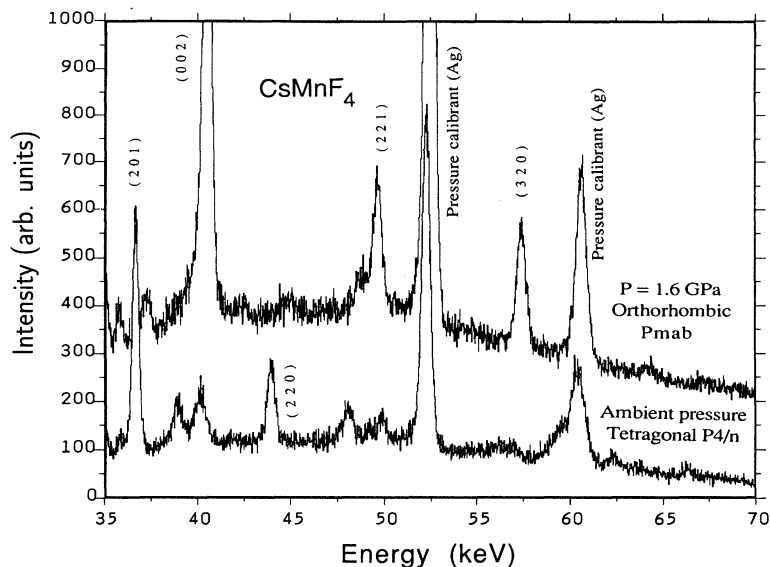


FIG. 1. Synchrotron x-ray diffraction patterns of CsMnF_4 at ambient pressure and at 1.6 GPa. Below 36 KeV only fluorescence peaks appear. Some relevant reflections, particularly $hk0$ ones, are depicted. $hk0$ reflections clearly differentiate between $P4/n$ and $Pmab$ space groups (see text for details).

is an order of magnitude worse than that obtained using monochromatic techniques. However, in this case we chose the EDPD method because we wished to survey the effect of pressure on CsMnF_4 across a large pressure range with fine sampling.

A diamond anvil cell was used to generate high pressures up to 8 GPa. Samples were mixed with Ag powder (which acted as an internal pressure calibrant) and ground to a homogeneous mixture before being loaded into the cell. An inconel metal gasket was used with a 0.2 mm sample hole, together with an ethanol-methanol-water mixture as the pressure transmitting medium.

The pressure cell used for the magnetic susceptibility experiments was attached to the drive rod of a Princeton Applied Research vibrating sample magnetometer, permitting measurements of the susceptibility as a function of temperature at a given pressure up to 1 GPa. Hydrostatic pressure was applied using binary beryllium-copper pressure cells, similar to those described by Guertin and Foner.⁸ The pressure transmitting fluid was Dow Corning 200 silicone oil with a viscosity of 300 stokes ($0.03 \text{ m}^2/\text{s}$) at 25 C.

The diffraction patterns collected at different pressures were analyzed in terms of crystal symmetry. Special care was taken due to the strong pseudosymmetry exhibited by most of the members of this layered-perovskite family of compounds. The very small difference that the unit cell parameters a and b exhibit within the AMnF_4 series for crystal symmetries smaller than tetragonal has been taken into account to determine the correct space group. For pressures higher than 1.5 GPa, reflections such as $hk0$ with $h+k \neq 2n$ appear systematically on all the diffraction patterns. These reflections are forbidden for the space group $P4/n$ but permitted for $Pmab$ symmetry. Therefore, when increasing pressure on CsMnF_4 a structural phase transition arises that reduces the symmetry of the system from the tetragonal space group $P4/n$ to the orthorhombic symmetry, space group $Pmab$ (see Fig. 1). The unit cell parameters and unit cell volume were determined as a function of pressure using the GENIE (Ref. 9) and PDPL (Ref. 10) computer packages.

The evolution of the unit cell volume of CsMnF_4 with the pressure is shown in Fig. 2, where the structural transition can be estimated to arise at the critical pressure of $P_c = 1.4 \pm 0.2$ GPa. With the limitations of the x-ray diffraction technique we are using here, RbMnF_4 can be well described at ambient pressure in the space group $Pmab$. Therefore, the crystal symmetry of CsMnF_4 at pressures as relatively low as 1.6 GPa corresponds well to that of RbMnF_4 at ambient pressure. Correspondingly, the unit cell volume of CsMnF_4 at P_c falls between unit cell volume values at ambient pressure of tetragonal CsMnF_4 and orthorhombic RbMnF_4 (366.7 \AA^3). No tetragonal symmetry is found for values of the unit cell volume of CsMnF_4 smaller than that of RbMnF_4 at ambient pressure (see Fig. 2).

From the magnetic point of view, a remarkable feature in

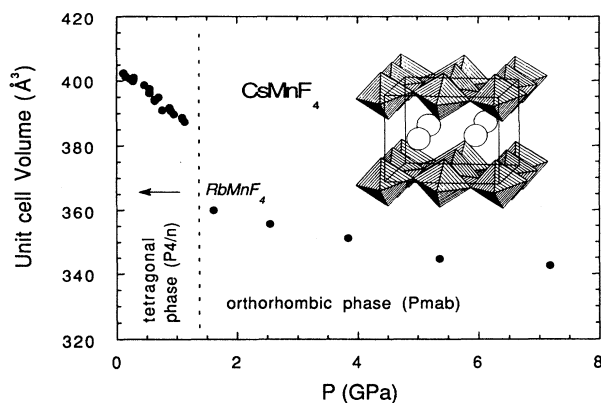


FIG. 2. Evolution with pressure of the unit cell volume of CsMnF_4 as determined from synchrotron x-ray powder-diffraction data. A structural phase transition takes place at 1.4 ± 0.2 GPa (see text for details). The arrow indicates the volume of the Rb derivative at ambient pressure. The inset shows the crystallographic unit cell at ambient pressure; open circles stand for the Cs atoms and octahedra for $[\text{MnF}_2\text{F}_{4/2}]^-$ units.

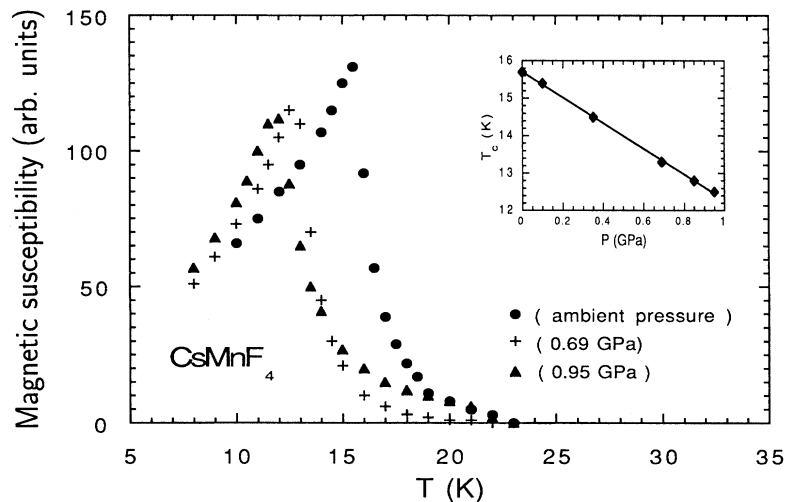


FIG. 3. Pressure and temperature dependence of the magnetic susceptibility of the ferromagnet CsMnF_4 at three different pressures. The inset shows the decrease of T_c with pressure.

this family is the ferromagnetic ordering of CsMnF_4 compared with the antiferromagnetic ordering exhibited by the other members of the series. This behavior is closely related to the value of the superexchange angle $\text{Mn-F}_{\text{eq}}\text{-Mn}$ within the layers. A value of $\alpha_c \approx 147^\circ$ has been determined as the critical superexchange angle at which the crossover between ferromagnetic ($\alpha > \alpha_c$) and antiferromagnetic ($\alpha < \alpha_c$) isotropic interaction takes place in this series.¹ On the other hand, a reduction in the unit cell volume should be accompanied by a decrease of the superexchange angle $\text{Mn-F}_{\text{eq}}\text{-Mn}$. This is clearly substantiated by magnetic susceptibility experiments as a function of the temperature and the external pressure on pristine powdered samples of CsMnF_4 . The temperature and pressure dependence of the magnetic susceptibility is depicted in Fig. 3 while the evolution of the critical temperature, T_c , with pressure is shown in the inset. The difference between the values of T_c determined from neutron diffraction or from susceptibility experiments at ambient pressure is due to the experimental differences in the form of assigning T_c . In the neutron diffraction experiments T_c was assigned extrapolating the temperature at which the intensity of the (001) magnetic Bragg peak vanishes,³ whereas in the susceptibility experiments T_c was assigned to the temperature at which the susceptibility diverges.

The critical temperature is proportional to $|\alpha - \alpha_c|$ since T_c scales with the isotropic magnetic interaction which can be written to first-order approximation as $J(\alpha) \propto (\alpha - \alpha_c)$. The dependence of T_c with the value of $(\alpha - \alpha_c)$ is shown in Fig. 4 for all the members of the AMnF_4 series. In the case of the Rb derivative the values of α observed in the directions of the two superexchange pathways within the layer, e.g., parallel to the a and b crystallographic axis, are different and give place to a ferromagnetic alignment of the moments in the a axes ($\alpha > \alpha_c$) and to an antiferromagnetic alignment in the b axis ($\alpha < \alpha_c$).¹ In Fig. 4 both values of $(\alpha - \alpha_c)$ have been represented with a bar. The type of magnetic alignment associated with each α value is also indicated in this figure. Since for the Cs derivative α is equal to $159.9(1)^\circ$, a reduction on the value of α implies a decrease of the value of $(\alpha - \alpha_c)$. Therefore, by ap-

plying external pressure on CsMnF_4 a decrease in T_c should arise. This is precisely what is observed in Fig. 3. Between ambient and 1 GPa, the evolution of T_c with pressure shows a linear behavior being (dT_c/dP) equals to -3.4 K/GPa. Unfortunately, the highest available experimental pressure in the susceptibility experiments was not enough to induce the expected magnetic phase transition. However, the above results are indicative that at pressures as relatively low as 1.6 GPa, CsMnF_4 should exhibit an antiferromagnetic ordering below T_c .

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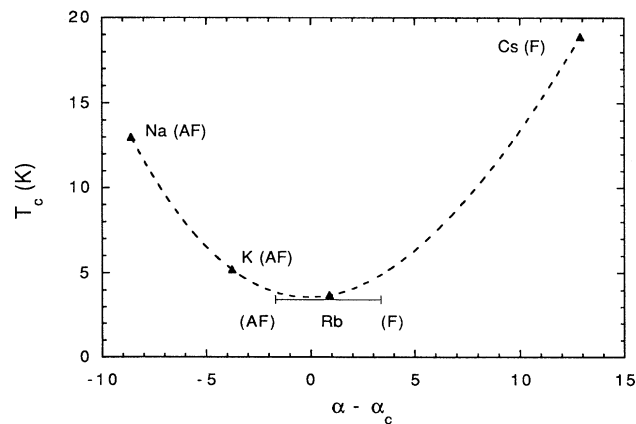


FIG. 4. Dependence of the magnetic ordering temperature with the value of $(\alpha - \alpha_c)$ for all the members of the AMnF_4 series. The two angles observed in the superexchange pathways of the Rb derivative are indicated with a bar while the dashed line is an eye guide. The type of magnetic alignment associated to each α value is also indicated (see text for details).

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